

THERMAL DECOMPOSITION OF AN IMPURE (ROXBURY) SIDERITE: RELEVANCE TO THE PRESENCE OF CHEMICALLY PURE MAGNETITE CRYSTALS IN ALH84001 CARBONATE DISKS K.L. Thomas-Keprta¹, S.J. Clemett¹, D.S. McKay², E.K. Gibson², S.J. Wentworth¹; ¹ESCG at NASA/Johnson Space Center, Houston, TX 77058; ²KR, ARES, NASA/Johnson Space Center, Houston, TX 77058; (kathie.thomas-keprta-1@nasa.gov)

Background and Introduction: The question of the origin of nanophase magnetite in Martian meteorite ALH84001 has been widely debated for nearly a decade. Golden *et al.* [1] have reported producing nearly chemically pure magnetite from thermal decomposition of chemically impure siderite [(Fe, Mg, Mn)CO₃]. This claim is significant for three reasons: first, it has been argued that chemically pure magnetite present in the carbonate disks in Martian meteorite ALH84001 could have formed by the thermal decomposition of the impure carbonate matrix in which they are embedded; second, the chemical purity of magnetite has been previously used to identify biogenic magnetite [2]; and, third, previous studies of thermal decomposition of impure (Mg, Ca, Mn)-siderites, which have been investigated under a wide variety of conditions by numerous researchers, invariably yields a mixed metal oxide phase as the product [e.g., 3-5] and not chemically pure magnetite. The explanation for this observation is that these siderites all possess the same crystallographic

structure (Calcite; $R\bar{3}c$) so solid solutions between these carbonates are readily formed and can be viewed on an atomic scale as two chemically different but structurally similar lattices. Hence solid solutions of the form (Fe_xMg_yMn_{1-x-y})CO₃ are possible over the entire compositional range between end-members (i.e., $0 \leq \{x|y\} \leq 1$ & $x+y = 1$) and thermal decomposition of chemically impure solid solution carbonate results in the formation of chemically impure ferrites [e.g., 3-5].

Methods: We undertook a study to determine the thermal decomposition products of chemically impure Roxbury siderite, which is a terrestrial analog for the Fe-rich carbonate component of ALH84001 carbonate disks. The bulk composition of Roxbury siderite, based on electron microprobe analyses at a spatial resolution of $\sim 1 \mu\text{m}$, is (Fe_{0.84}Mg_{0.10}Mn_{0.04}Ca_{0.02})CO₃ as reported by [6]. We employed two different heating regimes -- "slow" and "fast". The "slow" ($\sim 10^{-2}$ K/sec) regime is identical to that used by Golden *et al.* [1] while the "fast" ($\sim 10^8$ - 10^9 K/sec) regime used a pulsed CO₂

laser to simulate the rapid heterogeneous heating characteristic of impact shock.

Three separate sample fractions composed of small irregular fragments $< 500 \mu\text{m}$ in size were prepared by mechanical abrasion from the bulk sample. One fraction that was not heated served as a control. Both control and heated samples were subsequently embedded in epoxy and transmission electron microscopy (TEM) thin sections were prepared by diamond knife ultramicrotomy and analyzed by high resolution TEM.

Results and Discussion:

Control sample: HRSTEM characterization at the sub-micron scale of Roxbury siderite shows significant variations in Fe:Mg ratio relative to the bulk composition and appeared to be correlated with grain size. The fine grain ($< 100 \text{ nm}$) component is Mg-poor (Fe:Mg $> 20:1$) while, by comparison, the coarse grained component is Mg-rich (Fe:Mg $< 8:1$). In both size ranges Mn and Ca appeared relatively uniform in comparison.

"Slow" and "fast" heated samples: Under both "fast" and "slow" heating regimes, decomposition of Roxbury siderite resulted in the formation of impure ferrites with the Mg content of the impure ferrite varying from one crystal to another while the Mn content remained invariant. Since the Mg variation mirrors that of the unheated carbonate in magnitude and range this variation is simply a reflection of the initial content of the carbonate (notably, in neither the "fast" or "slow" products did we find any evidence for discrete MgO or CaO phases).

The only significant difference between the "fast" and "slow" heated samples was the degree to which the carbonate had undergone decomposition. In the "slow" heated sample no residual carbonate remained while in the "fast" heated sample only the very upper surface of the siderite exposed to laser beam underwent complete decomposition, while the underlying carbonate phase, although heavily vesiculated, contained no ferrites. *This observation is in sharp contrast to the magnetite rich rims and veins of ALH84001 disk-like carbonates that are characterized by an intimate mixture of magnetites embedded in a host carbonate matrix.*

These results support prior carbonate studies of extensive literature relating to the thermochemistry of the *Fe*-, *Mg*- and *Ca*-ternary carbonates [e.g., 3-5]. Thermal decomposition of impure, cation substituted siderite produces impure *Fe*-oxides. The chemical purity of the product ferrite phase and the temperature of decomposition are functions of the chemical purity of the reactant carbonate.

Copper Lake Siderite: Golden *et al.* [1] performed similar heating experiments with a natural siderite from Copper Lake, Nova Scotia, with an average composition of $(Fe_{0.643}Mg_{0.345}Mn_{0.012})CO_3$ with *Mg* ranging from ~32 to 44 mol%. Copper Lake siderite alone and in the presence of, but not mixed with, pyrite was heated to 623 K in evacuated, sealed tubes for nine days and allowed to cool to ambient temperature. The *Mg* composition of the magnetite produced from siderite ranged from ~4 to 10 mol% (ave. 7.1 mol%) and from ~0 to 5 mol% from the siderite plus pyrite. TEM samples were prepared by dissolution in 20% acetic acid. Golden *et al.* [1] suggest that for the siderite plus pyrite the resulting product “magnetite is chemically pure, yet...our experimental studies have high *Mg*” based on “the presence of relatively high *Mg* in acetic acid extracts” and conclude that “chemically pure magnetite can form in ALH84001 by the thermal decomposition of *Mg*-, *Fe*-carbonates.” However, since the natural siderite was not characterized by them prior to its decomposition and at the same scale used to analyze the resulting product phases, and only sample extracts were analyzed, the range in magnetite composition likely reflects the elemental heterogeneity of the natural siderite prior to decomposition.

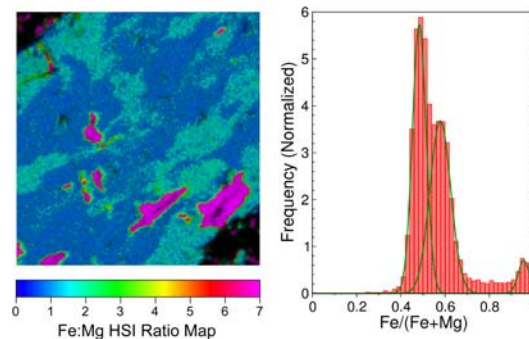
Heterogeneity of Copper Lake Siderite: While Golden *et al.* [1] did not determine the chemical heterogeneity of Copper Lake siderite, recent work by Bell [7] illustrates the variation of *Mg* and *Fe* abundances from the bulk in Copper Lake siderite using electron microprobe element mapping. Bell [7] reported at least three distinct carbonate compositions including nearly pure siderite with only minor to trace *Mg* (Figure 1). Therefore decomposition of Copper Lake siderite would occur in a number of stages, with increasing *T* corresponding to the successive decomposition of progressively more *Mg*-rich carbonate components. At 623K only the stability of the most *Mg*-poor, *Fe*-rich siderite would have been crossed resulting in the formation of a magnetite with low *Mg* abundances (i.e., nearly chemically pure magnetite)

although the bulk composition has much higher *Mg* abundances.

Implications for ALH84001: Thermal decomposition of Roxbury siderite under *both* “fast” and “slow” heating resulted in the formation of impure (*Mg*,*Ca*,*Mn*)-ferrites. These findings, which are supported by both kinetic and thermodynamic equilibrium modeling studies, are in stark contrast to the chemically pure magnetites characteristic of ALH84001 carbonate disks. Furthermore, two other populations of ALH84001 magnetite, those embedded within the *Fe*-free magnesite layer in which no high *Mg* magnetites have been reported (>1 mol% *Mg*) and those chemically impure magnetites with minor to trace amounts of *Cr* and/or *Al*, *could not* have formed by thermal decomposition of carbonate which contain neither *Cr* nor *Al*. We propose that the best model to describe the presence of a large fraction ALH84001 magnetite is deposition by allochthonous mechanisms which do not exclude a biogenic component.

In summary, experimental decomposition studies of natural siderite produce ferrites which reflect the composition of the original siderite – that is, heterogeneous precursor siderites form heterogeneous product ferrites.

Figure 1. *Left:* HSI ratio map of a polished section of Copper Lake siderite showing a range of compositions from *Mg*-rich (blue) to *Fe*-rich (pink) (adapted from [7]). *Right:* Frequency distribution of compositions from image on left shows three compositional groups comprise this siderite sample.



References: [1] Golden *et al.* (2006) *LPSC XXXVII*, #1199. [2] Bazylinski & Moskowitz (1997) in *Geomicrobiology: Interactions between Microbes and Minerals*, pp.181-223. [3] Jiménez López *et al.* (2008) *AGU*, # P51A-1405. [4] Gotor *et al.* (2000) *Phys. & Chem. of Min.* **27**, 495. [5] Gallagher and Warne (1981) *Thermochem. Acta* **50**, 253. [6] Lane & Christensen (1997) *JGR* **102**, 25581. [7] Bell (2007) *MAPS* **42**, 935.